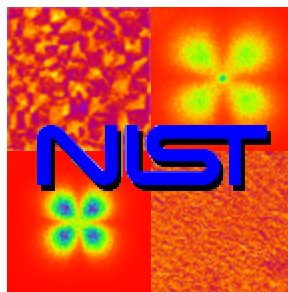


Co-crystallization and Shear-induced Structure in Polyolefin Blends

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and

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Outline

● Motivation and objectives

● Introduction

- Polyolefin copolymers
- Phase diagram

● Co-crystallization

- Small and Wide angle X-ray Scattering, DSC, TEM
- Model

● Shear-induced Structure

SAXS and Shear Light Scattering

● Summary and Future Work

Motivation and Objective

Motivation:

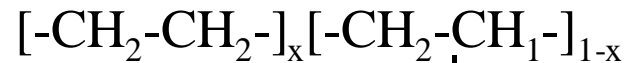
Processing, morphology and property relationship in polymer blends, especially blends of metallocene-catalyst based polyolefins.

Objective:

Investigate the interplay between the crystallization and liquid-liquid phase separation in a polyolefin blend;
Understand the structural change under shear.

The Polyolefin Statistical Copolymers

PEH: ethylene/hexene

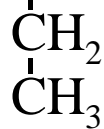
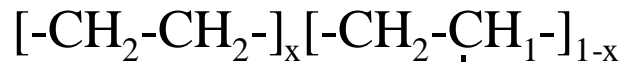


$$M_w = 110 \text{ k g/mol}$$

$$x = 0.98$$

$$\rho_{\text{branch}} : 9/1000 \text{ backbone C}$$

PEB: ethylene/butene



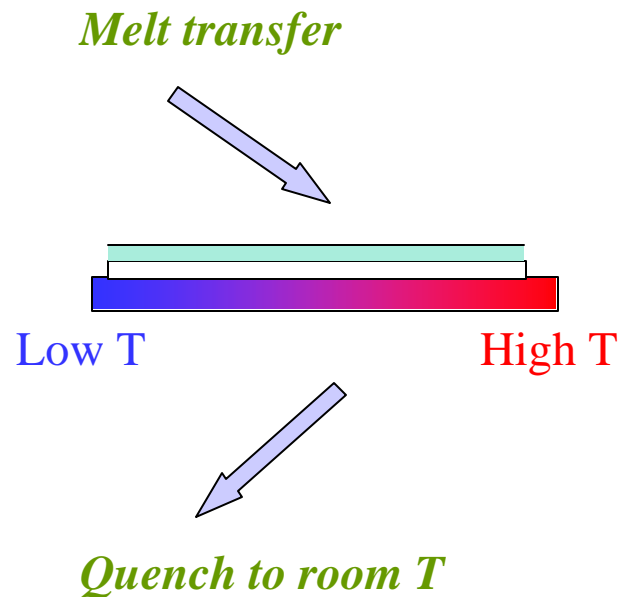
$$M_w = 70 \text{ k g/mol}$$

$$x = 0.85$$

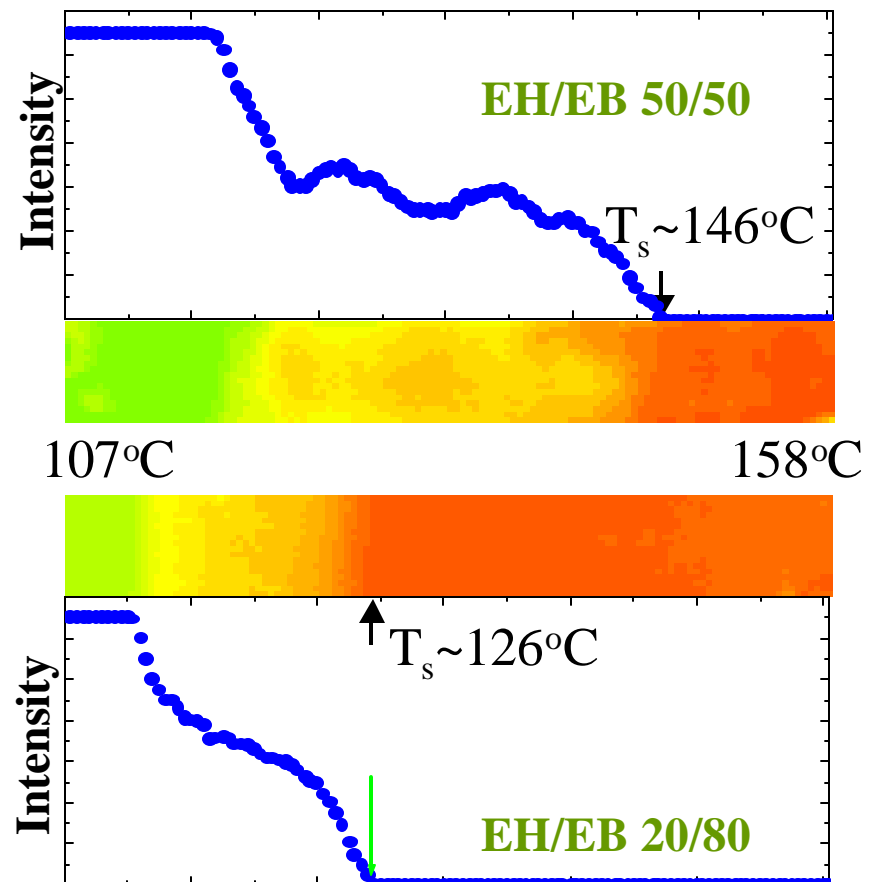
$$\rho_{\text{branch}} : 77/1000 \text{ backbone C}$$

Determining the liquid-liquid phase separation boundary:

Anneal a film of blend on a temperature gradient hot stage and quench to room temperature.

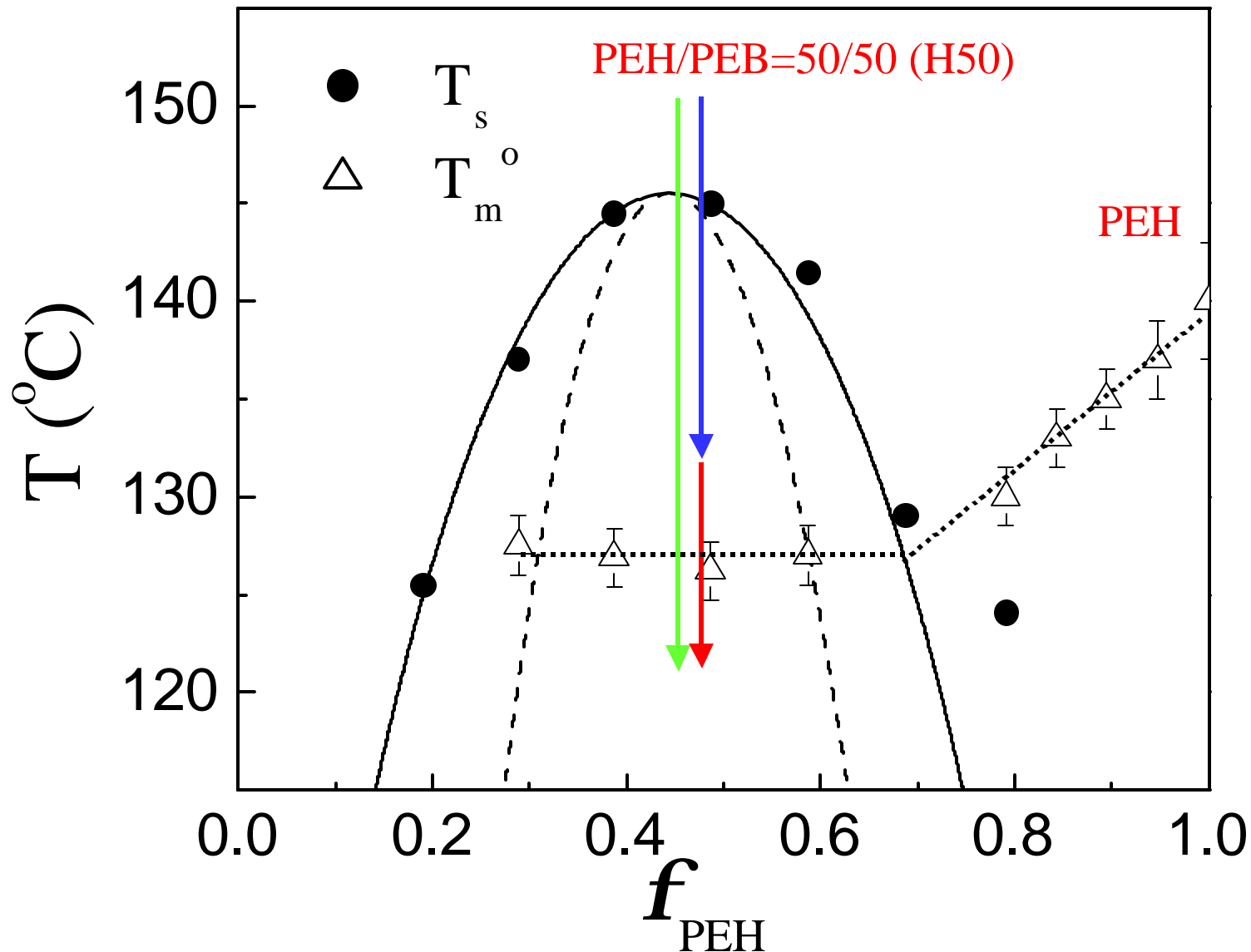


Characterization: photography

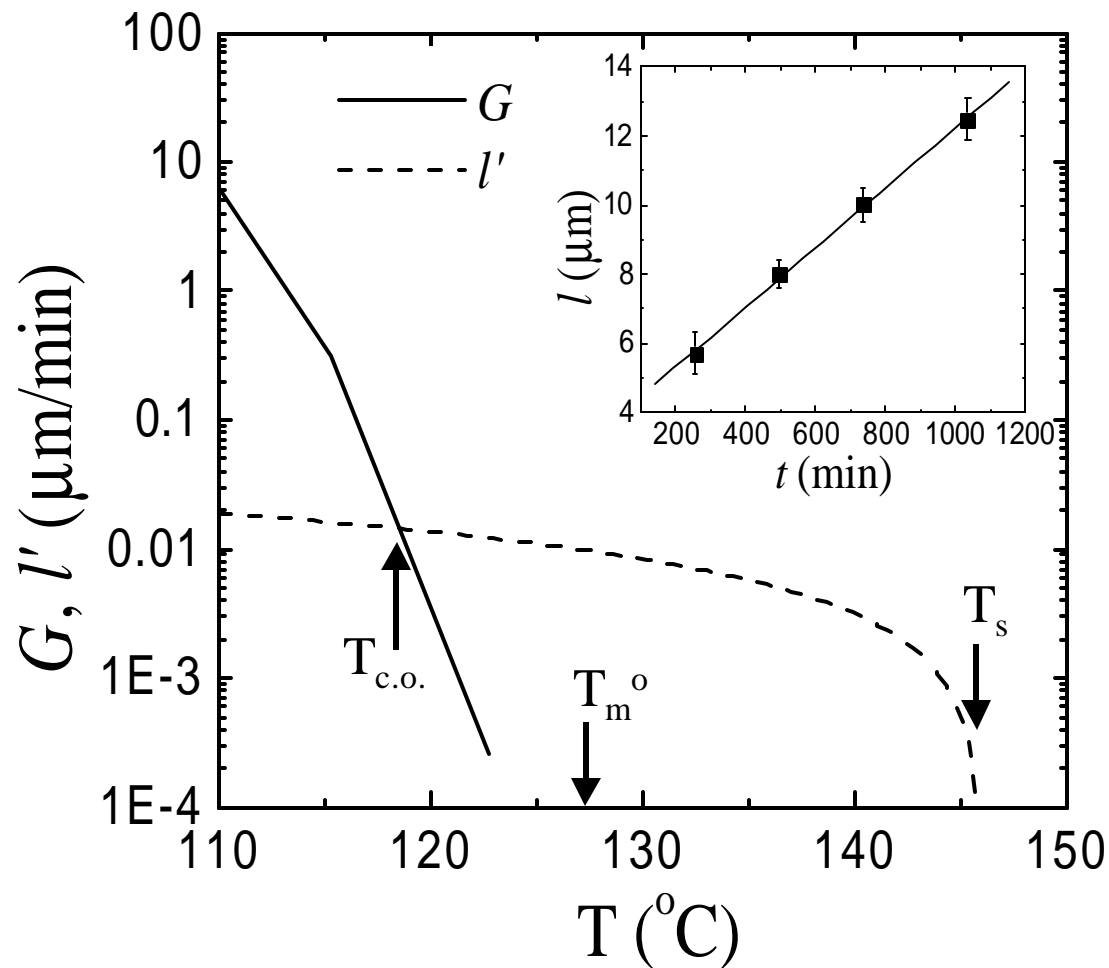


Phase Diagram of PEH/PEB Blend

($c = -1.1 \times 10^{-3} + 0.5/T$)



Competing growth rate and kinetics crossover



Scaling argument for the late-stage spinodal decomposition:

$$l \propto \frac{S}{h} t$$

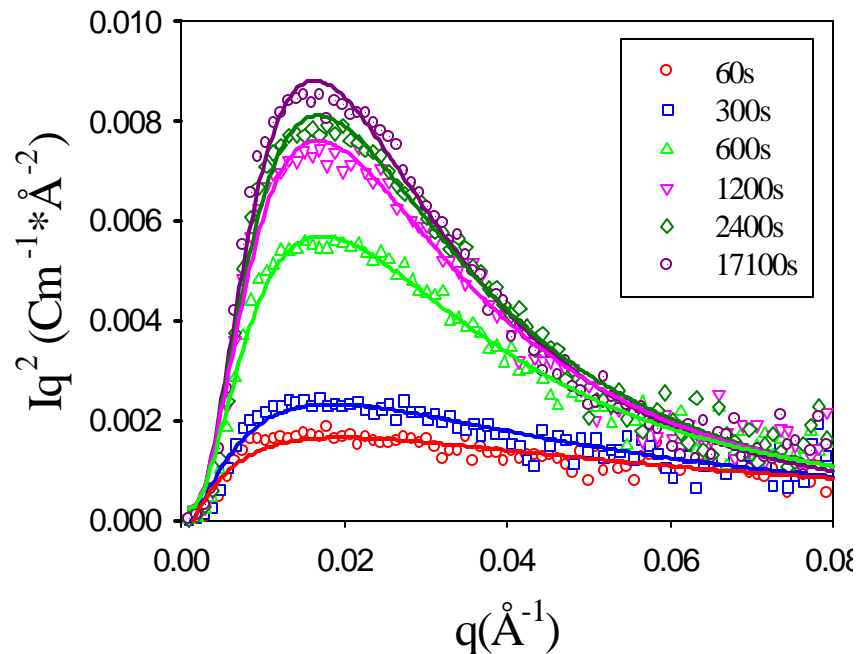
$$S \propto \frac{K_B T}{\mathbf{x}^{d-1}}$$

$$\tilde{t} = (T_s - T) / T_s$$

$$l' = \frac{l}{t} \propto \tilde{t}$$

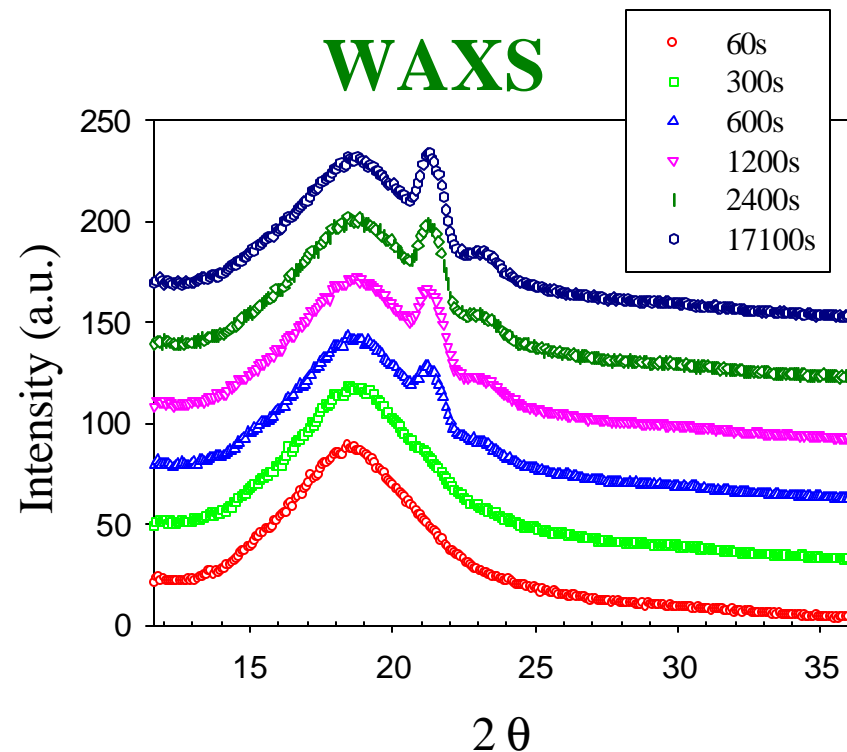
Simultaneous SAXS and WAXS during isothermal crystallization of H50 at 114 °C

SAXS



- Lamellae long period, L_m
- Scattering invariant, Q

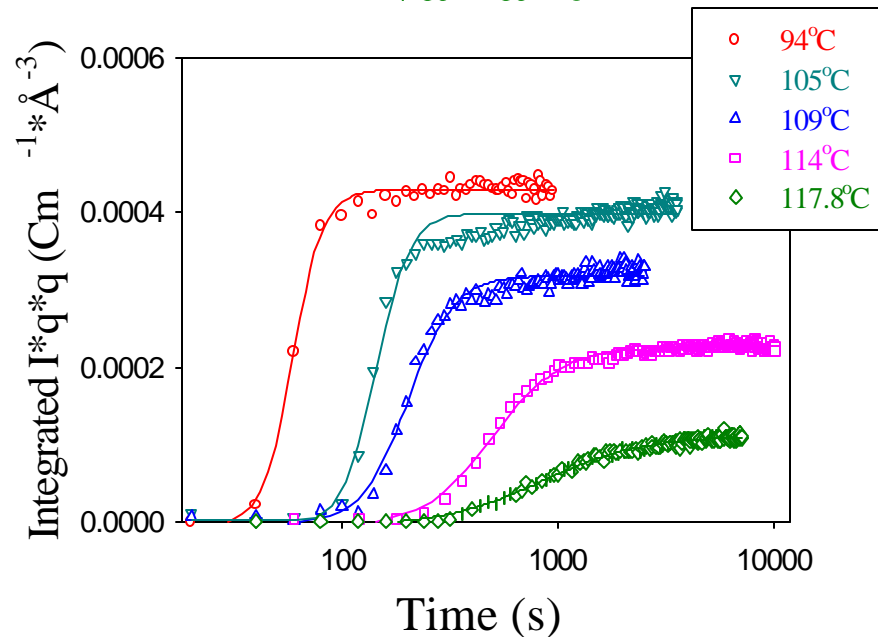
WAXS



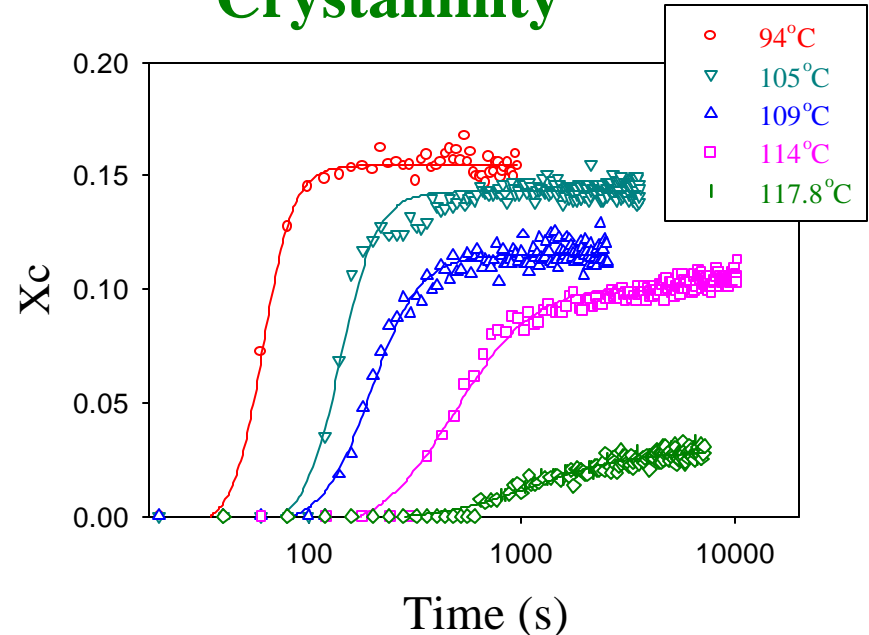
- Lattice parameters
- Crystallinity, X_c
- Amorphous inter-chain distance

Evolution of Q and X_c of H50 at various T_{iso}

Invariant

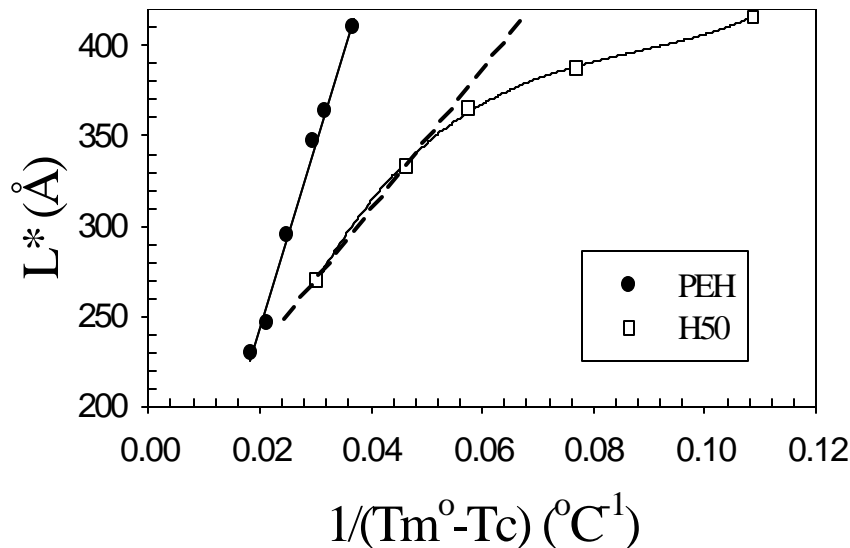
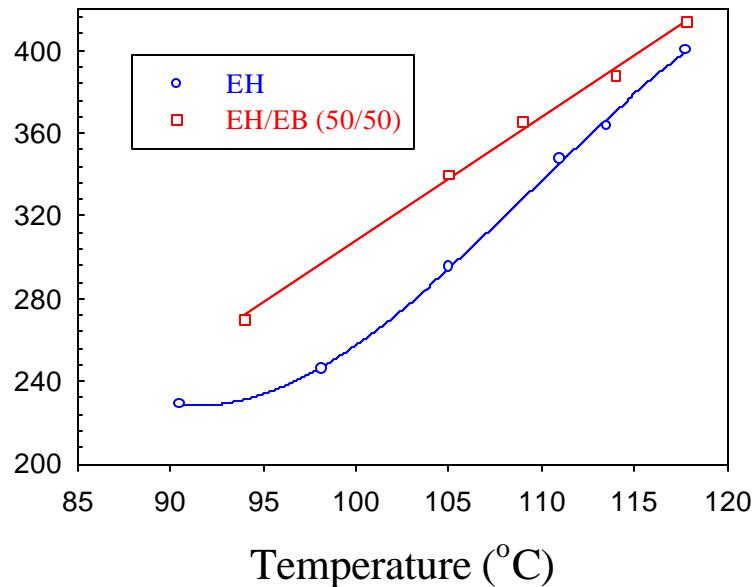


Crystallinity



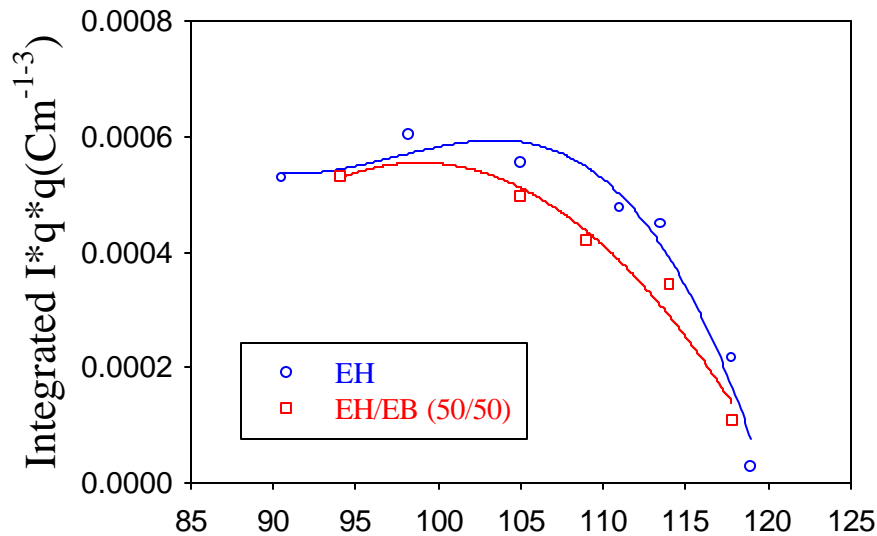
- Both Q and X_c display typical characteristics of the random copolymer crystallization, namely, a rapid primary crystallization followed by a slower process.
- The crystallization kinetics is consistent with microscopy study, and is analyzed using Avrami formalisms.

Final L_m of PEH and H50, a comparison

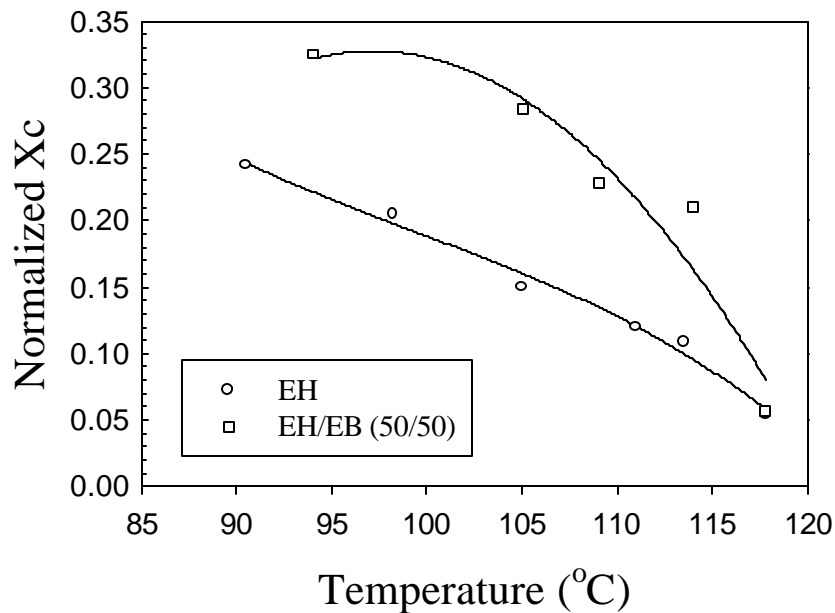


- $L_m(\text{PEH}) < L_m(\text{H50}) < 2 * L_m(\text{PEH})$ indicating partial segregation of PEB from the lamellar stack in H50.
- The difference of L_m between H50 and PEH decreases with increasing T_{iso} , which may be due to increasing liquid-liquid phase separation.
- The undercooling dependence of $L_m(\text{PEH})$ follows that of homopolymers, whereas that of $L_m(\text{H50})$ deviates significantly from this behavior.

Final Q_f , $X_{c,f}$ of PEH and H50, a Comparison



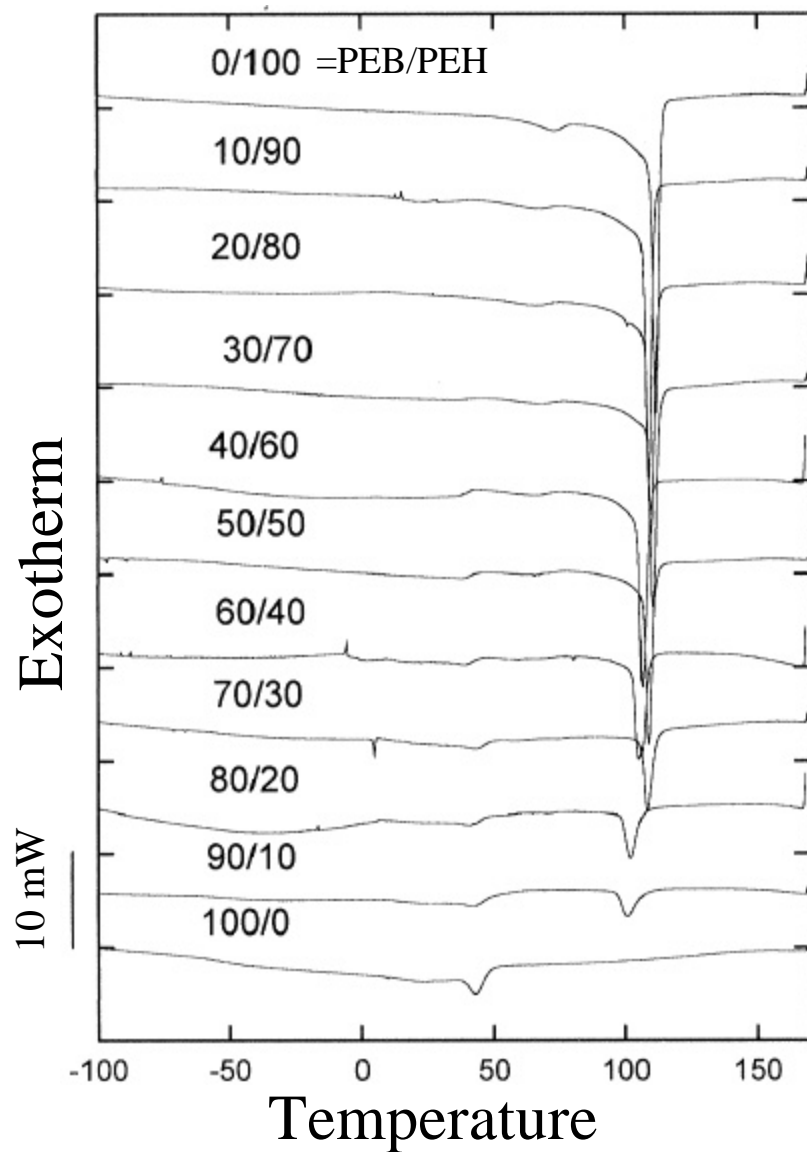
● $Q_f(\text{PEH}) > Q_f(\text{H50})$ only over a limited temperature range because of the competing effect of the lamellar thickness, crystal and lamellar stacking perfection, density difference between amorphous and crystals, etc. It is not clear whether the match at low and high T_{iso} is not accidental.



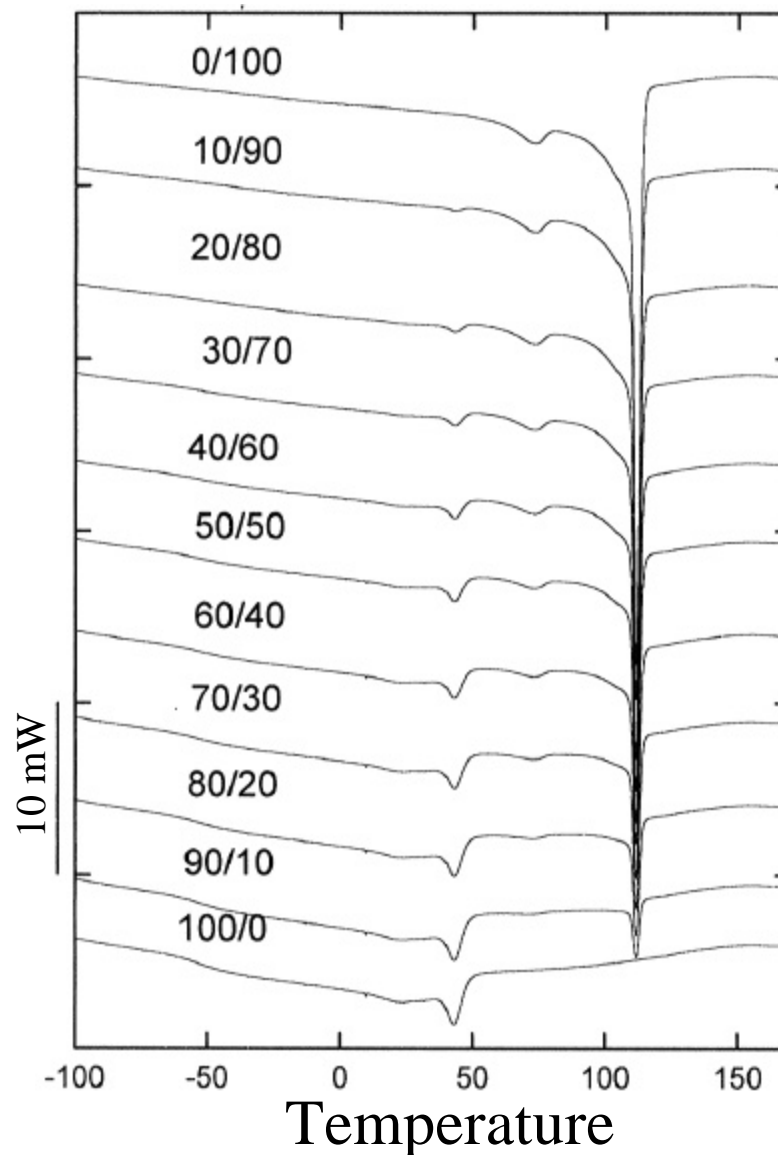
● Normalized crystallinity by the PEH content, $X_{c,f}(\text{H50}) > X_{c,f}(\text{PEH})$ indicates significant co-crystallization with long ethylene sequences of PEB in the blend.

DSC cooling scans on PEH/PEB blends

Blends of PEB/PEH

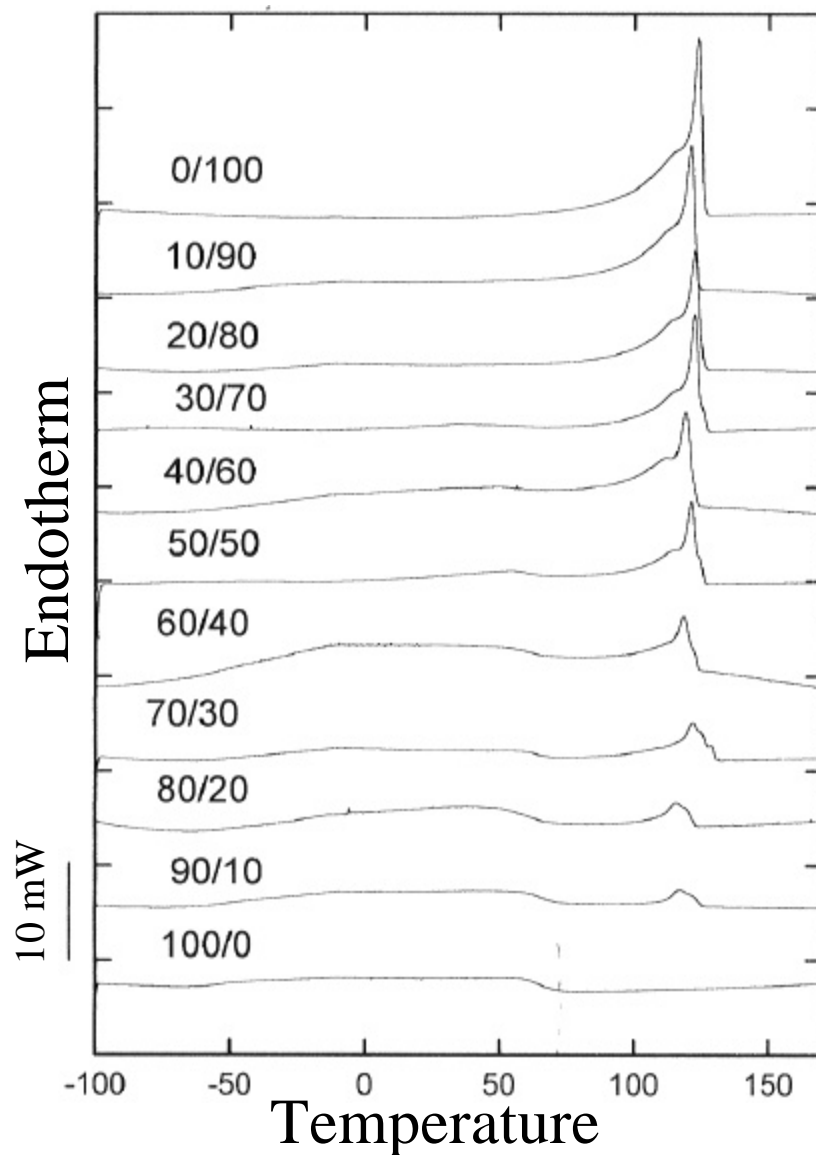


Lever rule calculation

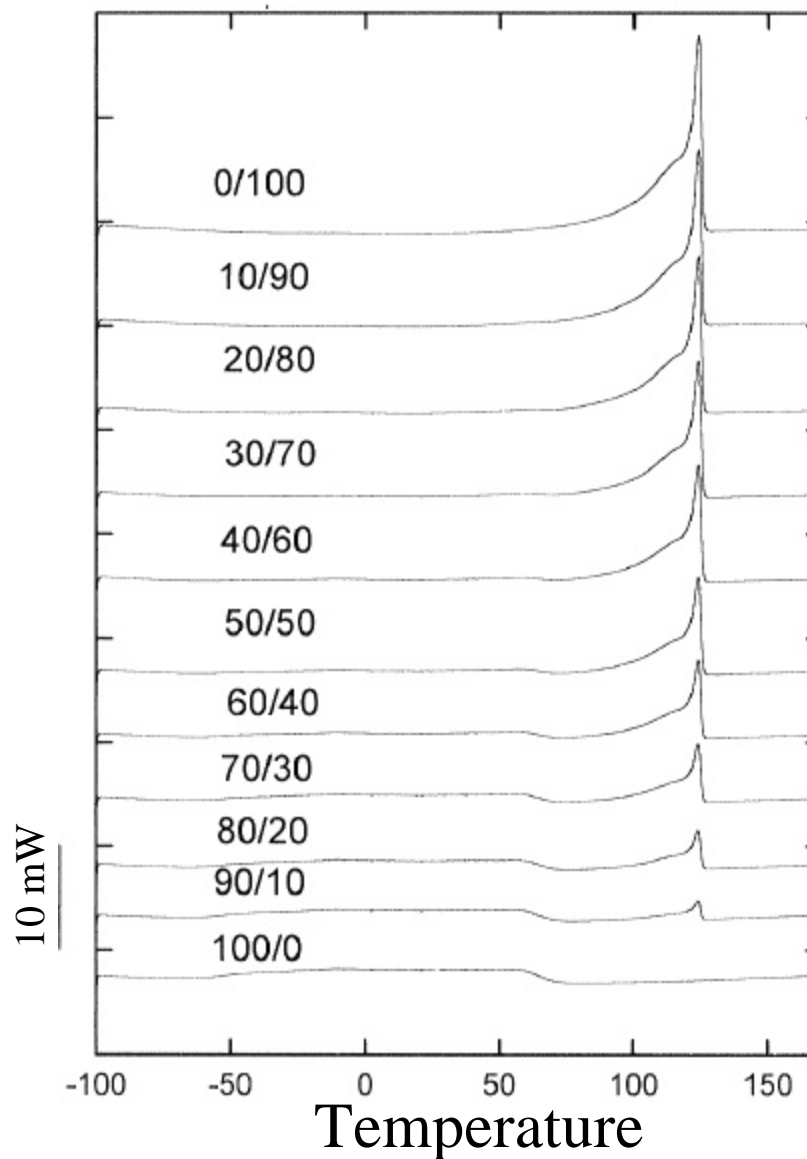


DSC heating scans on PEH/PEB blends

Blends of PEB/PEH



Level rule calculation



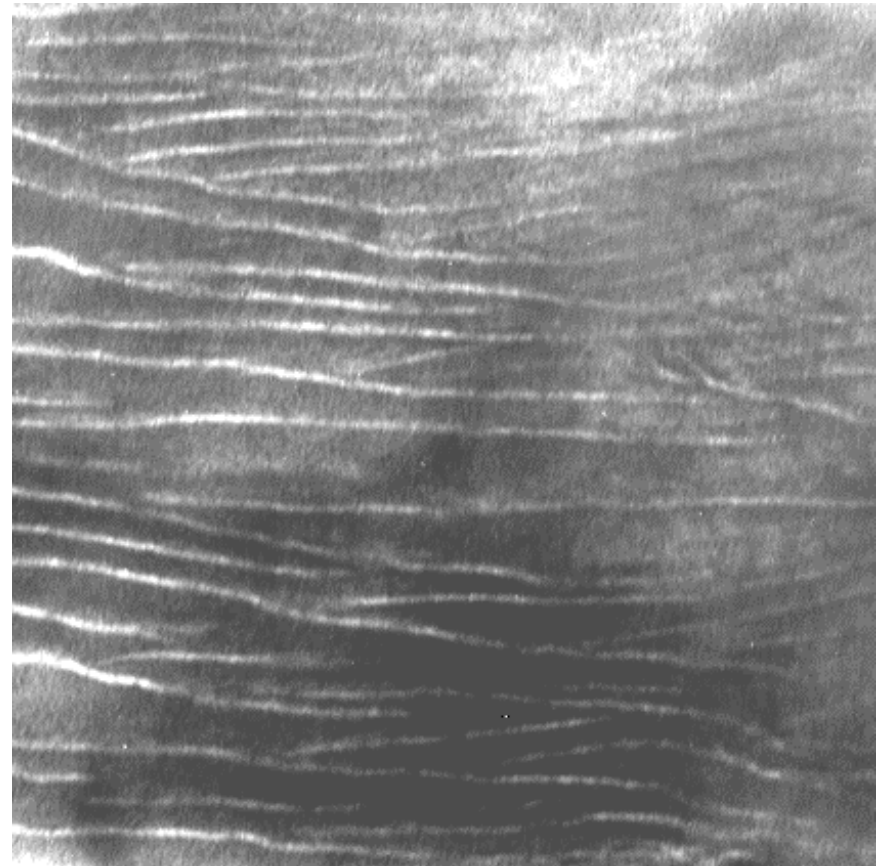
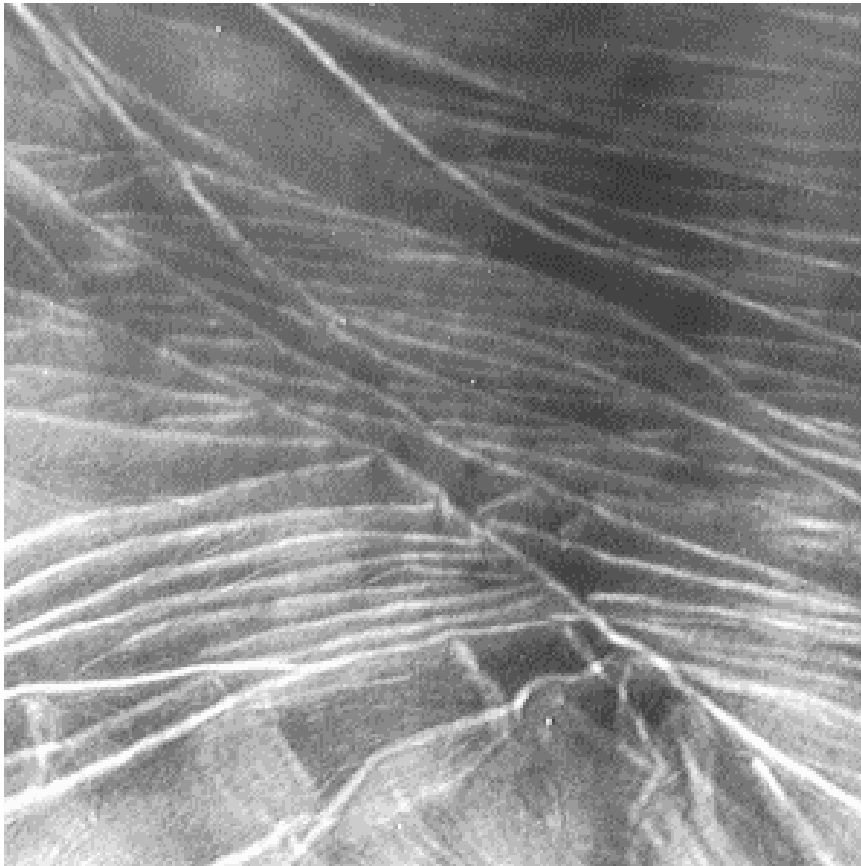
TEM studies on the lamellar structure

$T_{\text{iso}}=120^{\circ}\text{C}$ for 2 days, quench to water at room temperature

PEH

H30

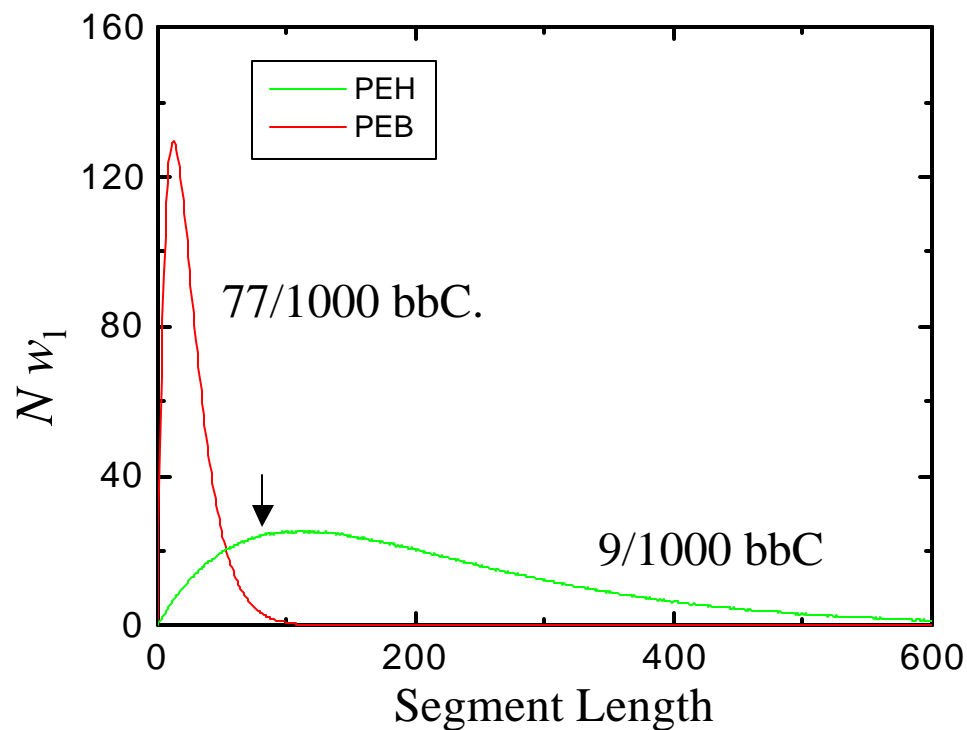
800 nm ~ 800 nm



200 nm

Weight distribution of ethylene sequence length

Random side-chain branch distribution in a single polymer chain



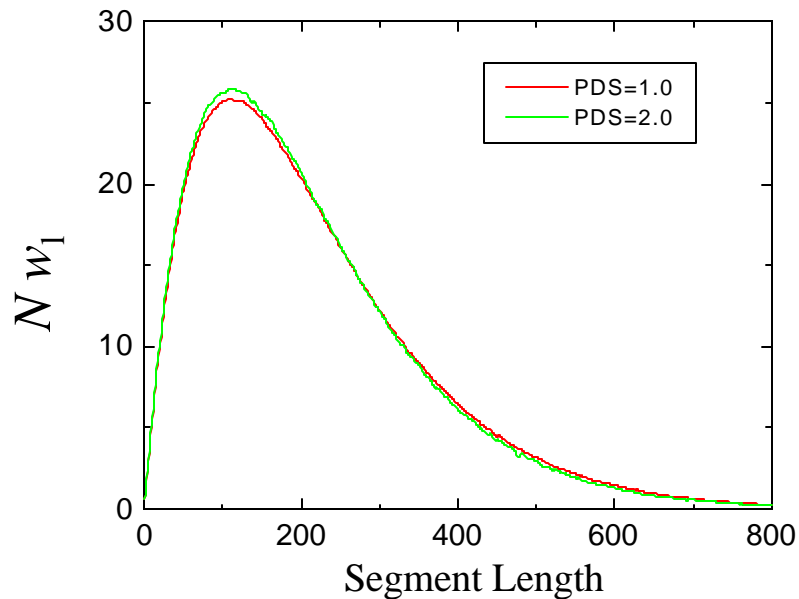
● Ethylene sequences display a length distribution depending on the overall branching density \mathbf{r}_0 .

● Crystallizable segments is determined by relation:

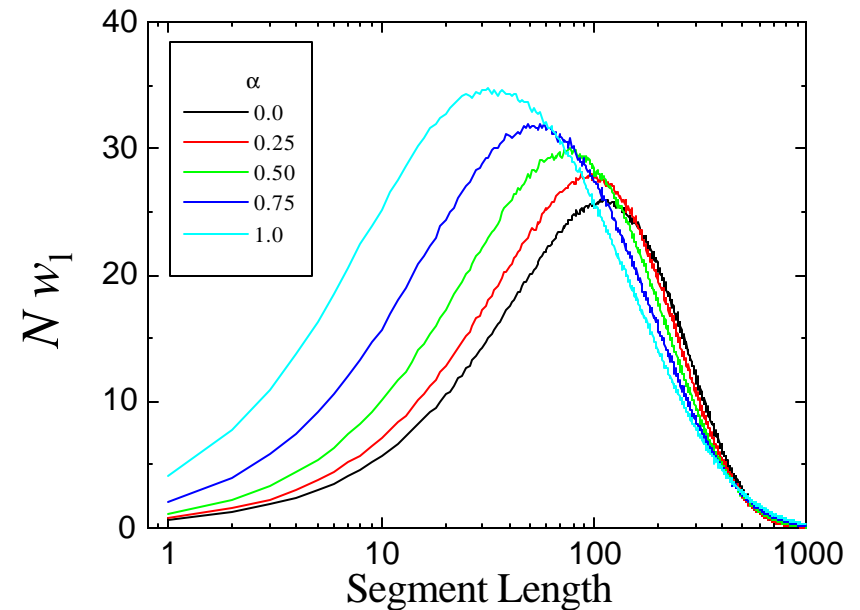
$$l^* = \frac{2s_e}{\Delta H_V} \frac{T_m^c}{T_m^c - T_c}$$

● Little overlap between PEH and PEB distributions.

The effect of polydispersity and inter-chain heterogeneity

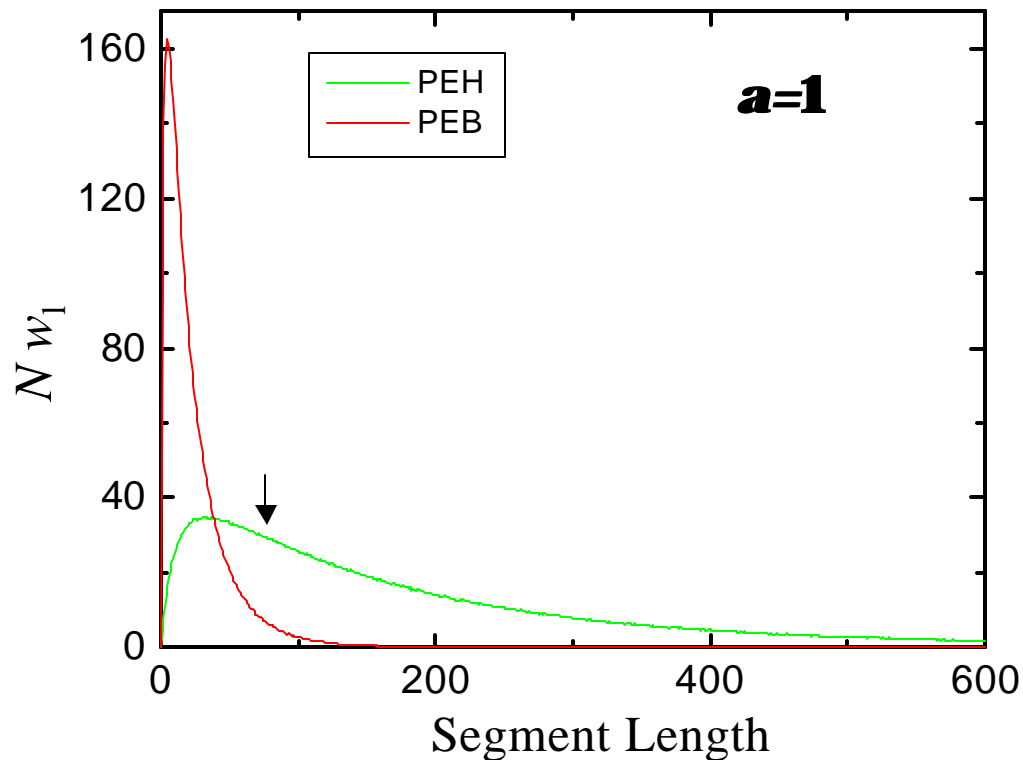


- No significant PDS dependence.
- Slightly narrower distribution in polydisperse polymers due to the smaller chain end effect.



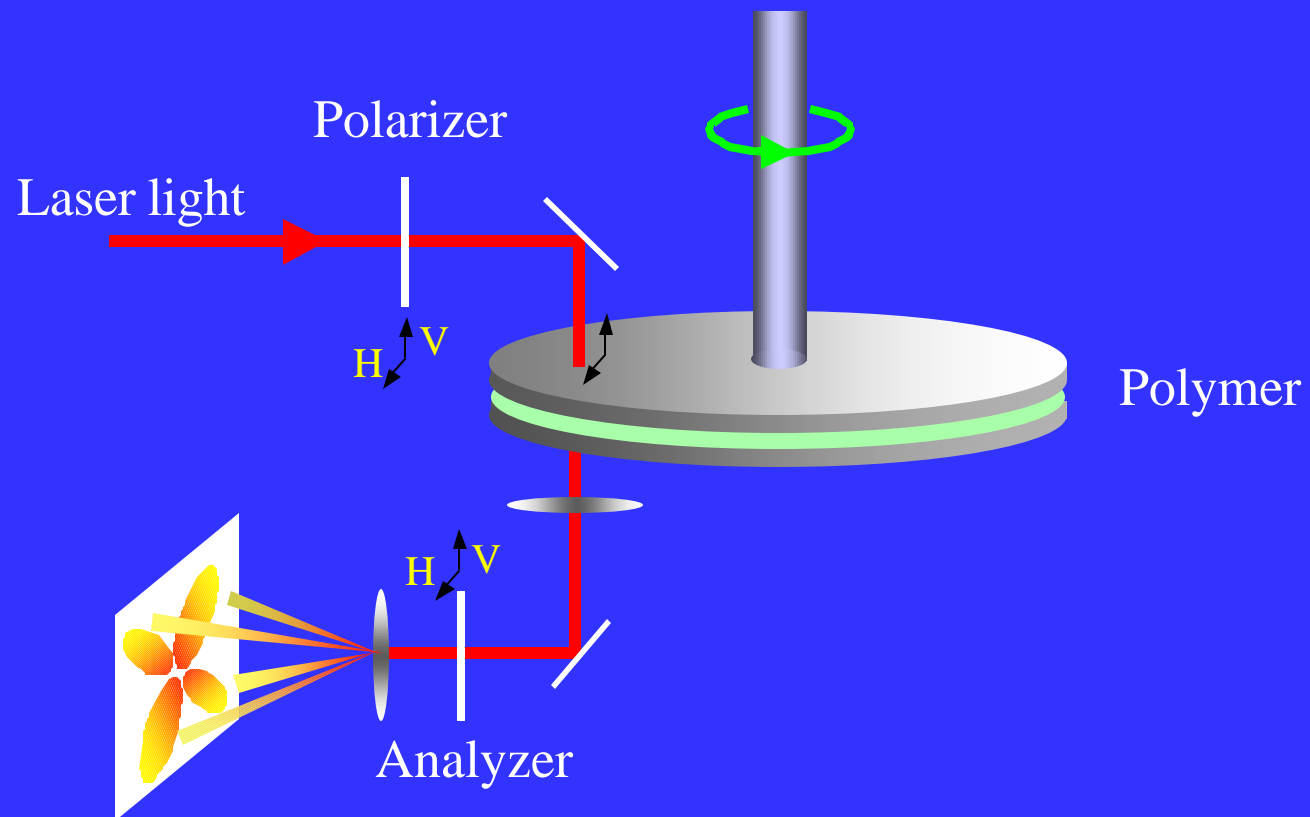
- Assuming inverse correlation between side-chain density and the molecular weight: $\mathbf{r} = \mathbf{r}_0 (M_w/M)^{\mathbf{a}}$
- Broader distribution with \mathbf{a} .
- Slight increase in long segments is balanced by significant amount of short chain segments.

PEH and PEB with inter-chain heterogeneity

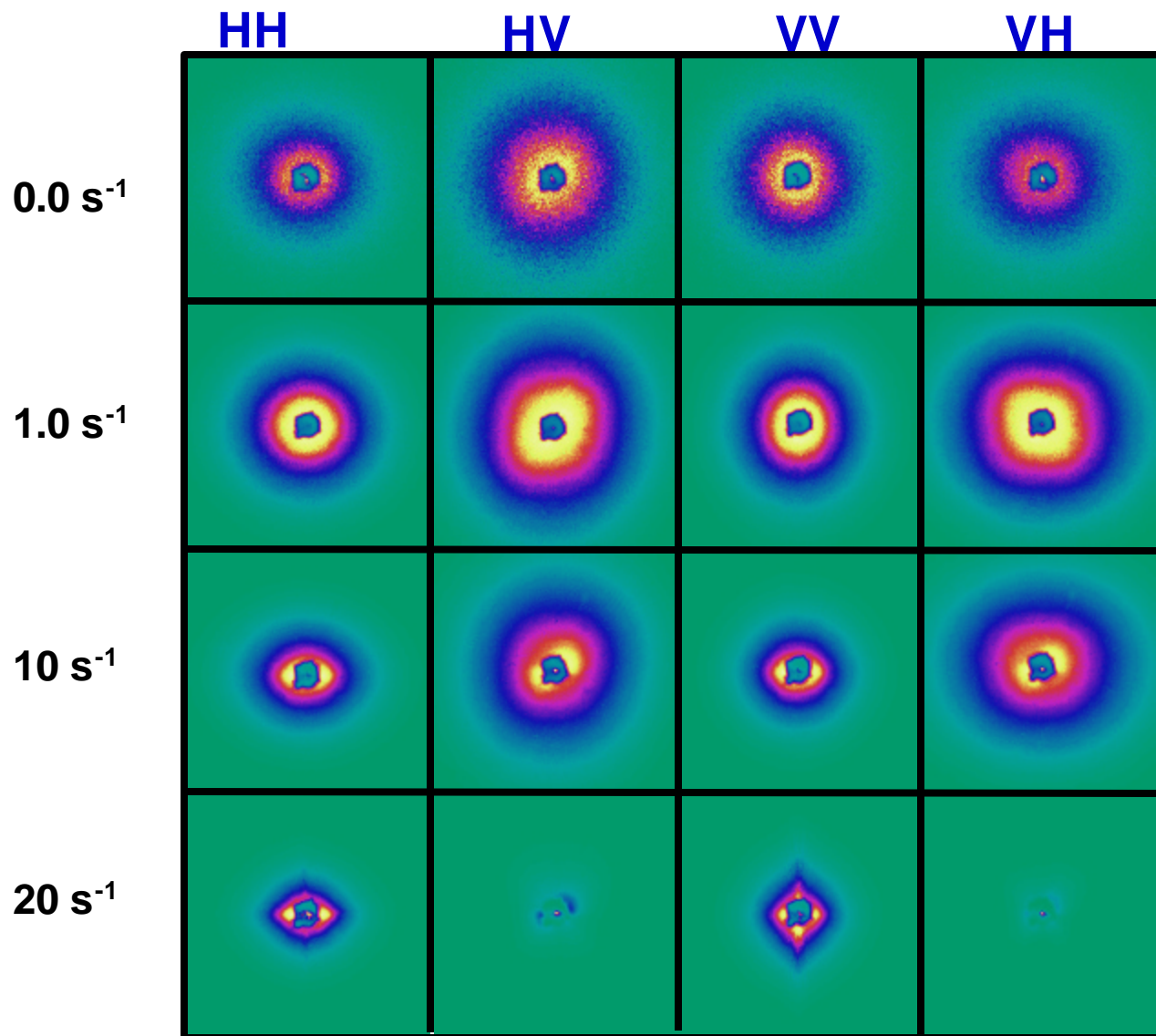


- Shift of segment length distribution in PEH causes significant overlap of the crystallizable sequences.
- This effect may not be necessary if the difference in \mathbf{r}_0 is small.
- The effect of intra-chain heterogeneity is yet to be investigated.

Shear Light Scattering (SLS) on Polyolefin Blends



SLS patterns of H10 at 121°C



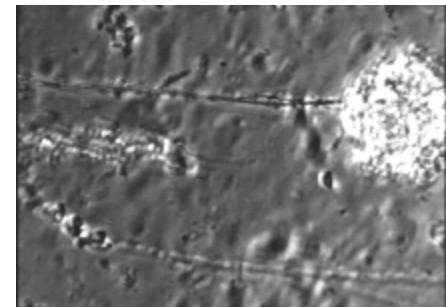
Shear direction requires additional polarizer/analyzer configuration.

At quiescence, crystals are randomly oriented.

At low shear rate, superstructural crystals orient giving rise to the isotropic scattering pattern.

At higher shear rate, lamella align along the vorticity.

At even higher shear rate, crystal superstructures dissolve, whereas the remaining crystals aggregate to form necklace.

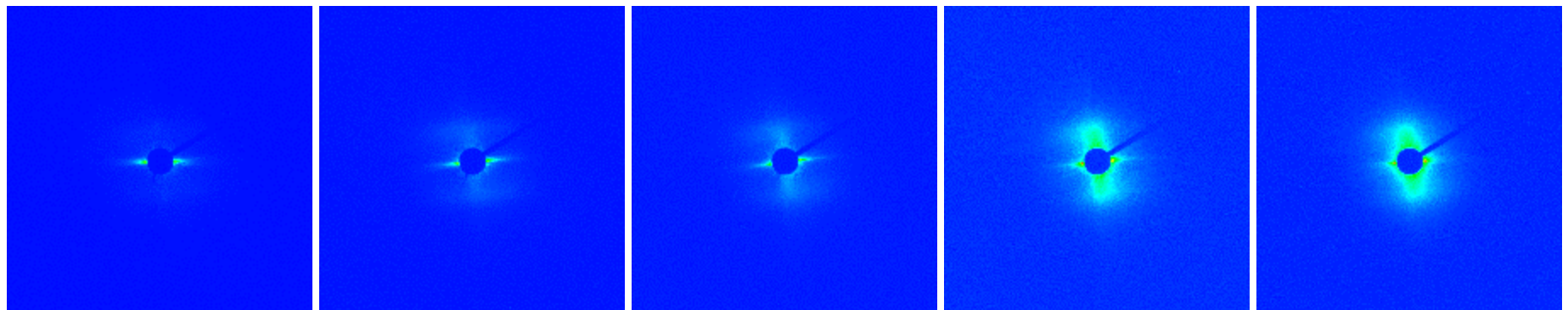


Summary

- **Isothermal crystallization kinetics and lamellar ordering has been measured using SAXS/WAXS.**
- **During isothermal crystallization of the blend, PEB partially segregates from the lamellar stacks, leading to a unusual undercooling-dependence of the long period.**
- **Both X-ray and DSC data point to the co-crystallization of long ethylene sequences of PEB in PEH crystals, which is further demonstrated by comparing 1- and 2-quench crystallization in a near critical blend.**
- **A calculation of ethylene sequence length distribution implies a possibility of the inter-chain heterogeneity causing the significant co-crystallization in this study.**
- **Simple shear flow can cause crystallites in melts to orient, deform and melt.**

2D SAXS Study of shear-induced crystallization

PEH, $T_c=115\text{ }^{\circ}\text{C}$, Strain 2000 %, rate 60 s^{-1}



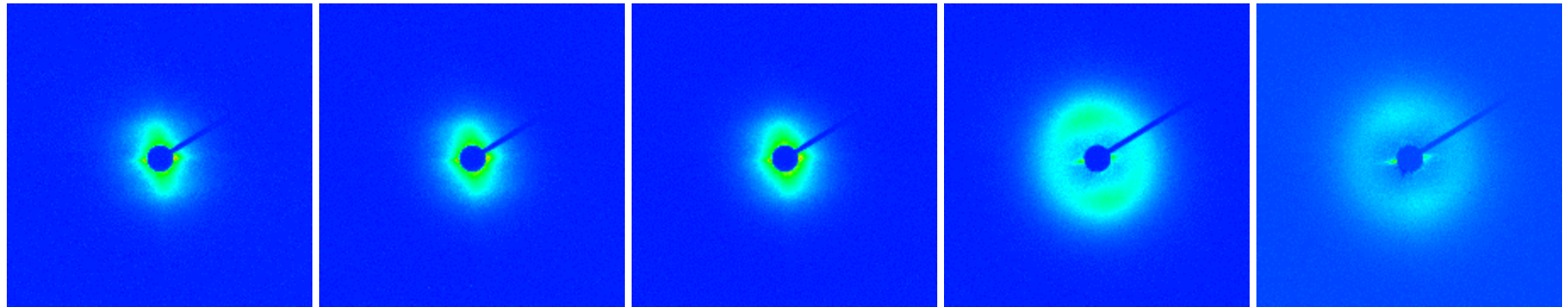
15 s

75 s

150 s

300 s

600 s



900 s

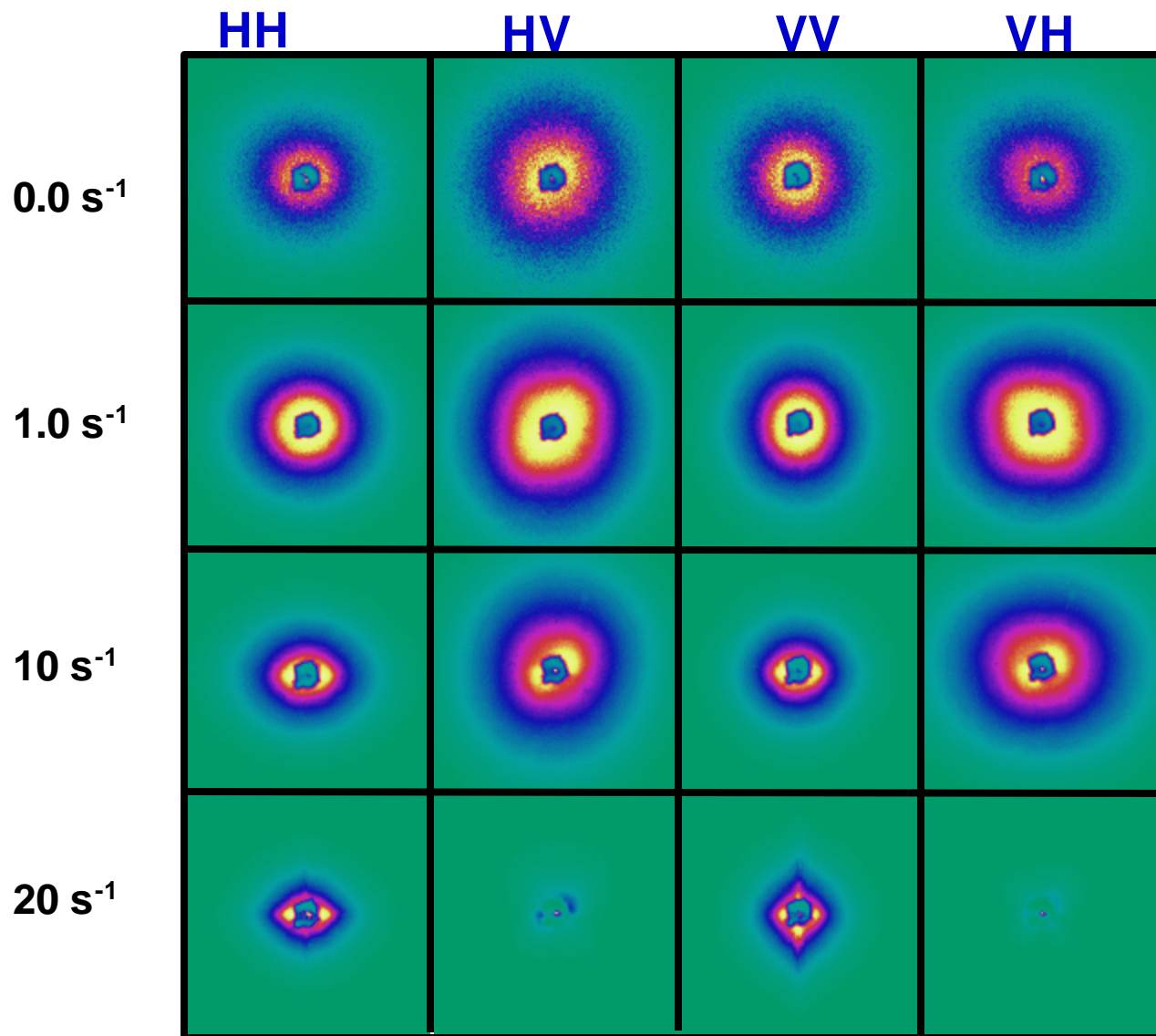
1200 s

1500 s

70 $^{\circ}\text{C}$

30 $^{\circ}\text{C}$

SLS patterns of H10 at 121°C



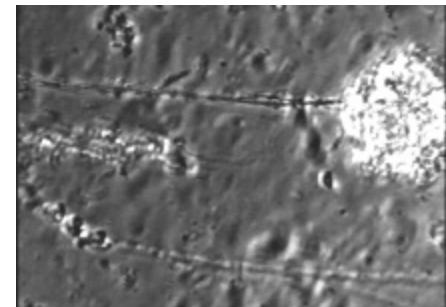
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PEH:PEOC: Phase Diagram

Poly(ethylene-co-hexene), PEH

$M_w = 110 \text{ kg / mol}$

$x = 0.98$ $\rho_{\text{branch}} = 1/57 \text{ backbone C}$

Poly(ethylene-co-octene), PEOC

$x = 0.86$ $\rho_{\text{branch}} = 1/15 \text{ backbone C}$

